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(54) LUBRICANT COMPOSITIONS

(71) We, THE PROCTER & GAMBLE COMPANY, a Company organised under the laws of the State of Ohio, United States of America, of 301 East Sixth Street, Cincinnati, Ohio 45202, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a lubricant composition comprising at least one diester of tripropylene glycol as a base fluid and an antioxidant, and to a lubrication process employing such a composition.

Dipropylene glycol dipelargonate has been sold as a base fluid for synthetic lubricant compositions. This material has a flash point that is too low for use in, e.g., jet lubricant compositions since at high temperatures too much of the fluid would be lost by evaporation. Also, although dipropylene glycol dipelargonate has a very low pour point, it solidifies when held at temperatures at which a lubricant should remain fluid. Thus, although it is a valuable lubricant base fluid it cannot be used in a process for lubricating two frictionally engaged surfaces over a wide range of temperatures from, e.g., −65°F or below to elevated temperatures.

Fatty acid diesters of dipropylene glycol have flash points that are too low for use as lubricants for the latest jet engines and both the dipropylene glycol and tetrapropylene glycol diesters become solid when held at low temperatures, e.g. about −65°F. Diesters of tripropylene glycol which contain two fatty acid residues containing less than 6 carbon atoms will degrade under extreme temperature conditions and esters containing fatty acids having 12 or more carbon atoms will tend to have pour points which are above about −25°F. Therefore, for use as a jet engine lubricant, it is required that one use diesters of tripropylene glycol wherein the fatty acids contain from 6 to 10 carbon atoms and only minor amounts of the fatty acids contain either 6 or 10 carbon atoms. Some small amounts of higher fatty acids can be present in the diesters, but in general they should be avoided. Synthetic fatty acids can also be used.

A tripropylene glycol diester lubricating base fluid, however, may be found somewhat unstable for use by itself in the high temperatures of the latest jet engines because of the hydrogen atom which is attached to a tertiary carbon atom in the tripropylene glycol chain. Accordingly, for use in jet engines, an effective antioxidant must be added to the tripropylene glycol diester lubricating base fluid.

The present invention provides a lubricant composition comprising at least one fatty acid diester of tripropylene glycol, wherein each fatty acid moiety contains from 6 to 10 carbon atoms, and from 0.001 to 5% by weight of an antioxidant that is a mixture of p,p[1]-dioctyldiphenylamine and N-phenyl-1,2,3,4-tetrahydro-2-naphthylamine.

The tripropylene glycol diesters to be used in the present invention may be prepared by the esterification of tripropylene glycol with fatty acids by conventional methods. The preferred diesters are those wherein each fatty acid group contains 7, 8 or 9 carbon atoms.

Suitable tripropylene glycol diesters are disclosed hereafter in the examples. Other auxiliary lubricating base fluids can also be used in combination with the essential lubricating base fluid of this invention. Suitable base fluids are hydrocarbon oils, fatty acid triglycerides and synthetic lubricants: these auxiliary base fluids are discussed further hereinafter.

The antioxidant used in this invention, as stated above, is a mixture of p,p[1]-dioctyl-

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diphenylamine and N-phenyl-1,2,3,4-tetrahydro-2-naphthylamine. Preferably the N-phenyl - 1,2,3,4 - tetrahydro - 2 - naphthylamine constitutes from 30% to 80% by weight of the said mixture, especially from 50% to 70%. It is most preferred that these two amines be used in a weight ratio of two parts of p,p'-dioctyldiphenyl amine to three parts N - phenyl - 1,2,3,4 - tetrahydro - 2-naphthylamine. A preferred level of the antioxidant is 1.5% by weight of the lubricant composition and a preferred range is from 0.1% to 2%.

It is believed that the p,p'-dioctyldiphenylamine acts (1) as a free radical inhibitor, (2) as a dispersant, and (3) in a secondary role as a base. It is believed that the N-phenyl-1,2,3,4 - tetrahydro - 2 - naphthylamine acts primarily as a base to neutralize any acid produced either in storage or in use.

Other additives which can be added to the compositions of this invention include viscosity index improvers, pour point depressants, dispersants, anti-wear additives and metal deactivators.

The viscosity index improvers are normally used at a level from 0.01% to 2% by weight of the lubricant composition. Suitable examples include polyisobutenes, polymethacrylates, vinylacetate-fumaric acid ester copolymers, and polyacrylates.

The pour point depressants are used at a level of from 0.01% to 2% by weight of the lubricant composition. Suitable pour point depressants are the aforementioned viscosity index improvers, alkylated waxes, naphthalenes, polymethacrylates and alkylated wax phenols.

The metal deactivators (anticorrosion additives) are normally used at a level of from 0.001% to 0.5% by weight of the lubricant composition. Suitable metal deactivators include: disalicylidene-1,2-diaminepropane; benzoguanamine and N-alkyl and ring alkyl substituted benzoguanamines; thioureas; octadecyl amine; quinizarin; quinolines; phenylacridine; hexamethylenetetramine; thiobenzamide; benzothiazole; and imidazoline.

The anti-wear additives are normally used at a level of from 0.01% to 5% by weight of the lubricant composition. Suitable anti-wear additives include tricresylphosphate, organic phosphites, and dialkyl mono- and di-halomethane diphosphonates in which the alkyl groups have from 1—22 carbon atoms.

Dispersants are normally used at a level of from 0.01% to 2% by weight of the lubricant composition. Suitable dispersants include: The aforementioned viscosity index improvers, copolymers of methacrylates or acrylates; N-substituted long chain alkenyl succinimides; high molecular weight esters or polyesters; and vinylacetate-fumaric acid ester copolymers.

Other suitable additives are disclosed in Canadian Patent 792,739.

The essential fatty acid diesters of tripropylene glycol can be combined with other known lubricating base fluids to improve their properties. Broadly, the other base fluid can be either a petroleum hydrocarbon, a fatty acid triglyceride, a synthetic fluid, an aqueous base fluid, or mixtures thereof. Petroleum hydrocarbons include mineral oil (including light solvents, neutral oils, heavy, bright and refined stocks, and asphaltic residual stocks), greases and waxes. The lubricating base fluid can also comprise suspensions of graphite in oils. Synthetic fluids include such disparate materials as polymerized olefins, organic carbonates, organic esters and/or ethers, polyglycols, silicones, modified organic materials (halogenated, phosphates, sulphurized, etc.) polymers, e.g., alkylmethacrylate polymers and synthetic resins, e.g., resins formed by esterification of polyhydric alcohols with polycarboxylic acids. Examples of base fluids which can be used in the practice of this invention include those disclosed in U.S. Patent 2,599,761, especially columns 9—11; U.S. Patent 2,725,359, especially columns 2, and 7—8; U.S. Patent 2,767,142, especially column 4; U.S. Patent 2,882,228, especially columns 6—7; U.S.Patent 2,956,952, especially columns 3—5; U.S. Patent 2,993,859, especially columns 2—3; U.S. Patent 3,296,138, especially columns 6—10 and 12—20 and U.S. Patent 3,357,920, especially columns 5—7. Other suitable lubricating base fluids are disclosed in "Encyclopedia of Chemical Technology", Kirk-Othmer, second edition, volume 12, pages 557—616, especially pages 576—582, Interscience Publishers, 1967. More examples of metal working lubricant base fluids can be found in "Metal Working Lubricants", E.L.H. Bastian, first edition, McGraw-Hill Book Co., Inc., 1951.

Especially preferred in such mixtures are (1) other esters of polyols, and monobasic acids such as C_6—C_{12} fatty acid polyesters of ethylene glycol, polyethylene glycols, propylene glycol, other polypropylene glycols, neopentyl glycol, trimethylol ethane, trimethylol propane, and pentaerythritol; (2) dibasic acid esters, such as C_6—C_{12} fatty alcohol (including normal, branched and secondary alcohols) esters of adipic, azelaic, and sebacic acids; and (3) complex esters such as polyalkylene glycol dibasic acid polyesters terminated with either a monobasic acid or a monohydric alcohol.

Two types of lubricating base fluid mixtures are of special importance. These are fluids which are designed to meet United States military specifications MIL-L-7808 G and MIL-L-23699A. The first specification (MIL-L-7808G) requires a low pour point

and good wear characteristics. The C_6—C_{10} fatty acid diesters of tripropylene glycol are superior lubricating base fluids for preparing lubricant compositions to meet this specification which requires a low pour point and good wear characteristics. However, small amounts, usually less than 50% of some of the diesters of dibasic acids, e.g., dioctyl adipate or di(2-ethylhexyl) sebacate can be used in combination with the superior tripropylene glycol diesters. The resulting lubricant compositions can be more economical although they will not be as good as lubricant compositions containing only the tripropylene glycol diesters.

The second specification (MIL-L-23699A) requires a lower rate of evaporation, a higher viscosity, and a higher degree of thermal stability than can be obtained with the tripropylene glycol diester by itself. However, if small amounts, usually less than about 50% of the tripropylene diesters are added to such fluids as trimethylol propane tripelargonate or pentaerythritol tetraesters such as those described in U.S. Patent 3,360,465, one can lower the pour point of the lubricating composition and improve its wear characteristics without increasing the evaporation rate and decreasing viscosity to an unacceptable degree.

This invention further provides a process of lubricating two frictionally-engaged metal surfaces which comprises disposing between the said metal surfaces a lubricant composition of the present invention. This process can be used over a wide range of temperature, even at −65°F or below (depending upon the actual composition of the lubricant).

Lubricant compositions provided by this invention have been found to have acceptable flash points, freezing points and load-bearing characteristics for use as jet engine lubricants.

The compositions of this invention are also capable of being used with good results as automotive crankcase lubricants, transmission fluids, low temperature greases, lubricants for sintered bearings, steam turbine engine lubricants, textile lubricants, metal polishing lubricants (especially aluminium), brake fluids, metal working lubricants, lubricants for vacuum pumps, lubricants for two and four cycle engines, e.g. lawn mowers, lubricants for sealed lubricant systems, hydraulic fluids in general, and automotive and truck turbine engines.

The following examples are illustrative of the lubricant compositions of the invention.

EXAMPLE I.

In this and the subsequent examples, all pour points are determined according to ASTM D97. The corrosion and oxidation stability tests were a modification of the Federal standard 791, Method 5308 wherein the tests were run at 347°F. The evaporation test was ASTM D972.

The following compares a tripropylene glycol diester wherein the fatty acids have the substantially following distribution C_6-4%; C_8-55%; C_{10}-40%; and C_{12}-1% and the same tripropylene glycol diester in a lubricant composition containing 1.5% of an antioxidant which is 40% p,p[1]-dioctyldiphenylamine and 60% N-phenyl-1,2,3,4-tetrahydro-2-naphthylamine.

A. Oxidation — Corrosion Test (347°F).

	(1) % Volume Loss	(2) Total Acid Number
Tripropylene glycol diester (TGP) ...	23	24
Tripropylene glycol diester and antioxidant	2	0.55

(3) *Corrosivity (weight loss mg./cm²)*

	Al.	Mg.	Cu.	Steel	Ag.
TPG		Too bad to run.			
TPG + antioxidant ...	0.000	0.008	0.188	0.015	0.008

B. % Evaporation 6½ hours at 400°F.

TPG	57
TPG + antioxidant ...	15

The TPG alone lost an excessive amount of material in both the oxidation-corrosion and evaporation tests and the acid value became excessive, whereas with the antioxidant system there was minimal loss in both tests and the acid value was acceptable. It can be seen from the above data that, surprisingly, an antioxidant is conducive to the good performance of the composition in respect of corrosivity, evaporation, and acid number.

Pour points were determined for various diesters of polyalkylene glycols as follows:

Diester		Pour Point (°F.)
(1)	Tripropylene glycol dilaurate	−25
(2)	Tripropylene glycol dicaprate	−59
(3)	Tripropylene glycol dipelargonate	−90
(4)	Tripropylene glycol dicaprylate	−100
(5)	Tripropylene glycol diheptanoate	−100
(6)	50:50 mixture of (2) and (4)	−80
(7)	Tripropylene glycol diester wherein the fatty acyl content, randomly distributed, is approximately 4% C_6; 55% C_8; 40% C_{10} and 1% C_{12}	−89
(8)	(3) prepared with synthetic fatty acids	−85
(9)	Tripropylene glycol diester with random C_9 fatty acids	−65
(10)	Diethylene glycol dipelargonate	35
(11)	Diethylene glycol dipelargonate (prepared from synthetic fatty acids)	−10
(12)	Triethylene glycol dipelargonate	15
(13)	(12) prepared with synthetic fatty acids	−5
(14)	Tetraethylene glycol dipelargonate	25
(15)	(14) prepared with synthetic fatty acids	−20
(16)	Tripropylene glycol dibenzoate	0
(17)	Dipropylene glycol dicaprate	−75
(18)	Tetrapropylene glycol diester (n-C_7—C_{10} fatty acids—Average $C_{8.0}$)	−55
(19)	Tripropylene glycol diester (n-C_7—C_{10} fatty acids—Average $C_{8.6}$)	−85

Of the above esters and ester compositions, those numbered 10 to 18 inclusive are not examples of the invention and are included for comparison only.

When diesters 17, 18 and 19 were held at −65°F. for 72 hours, both 17 and 18 became solid whereas diester 19 retained a viscosity of about 9200 centipoises. This shows unusual low-temperature viscosity stability for the diesters of this invention as compared with the dipropylene glycol and tetrapropylene glycol analogues. In Shell four ball tests at 40 kg. weight and 130°F. 17, 18 and 19 gave acceptable wear scars of 0.57, 0.54, and 0.51 respectively. 17, 18 and 19 were acceptable in Ryder Gear tests also, giving values of 2100, 2500 and 2900 ppi respectively. These materials also had Viscosity Indices of 130, 143 and 30 respectively.

As can be seen from the above data many compounds which are quite similar to the essential tripropylene glycol diesters of this invention have surprisingly higher pour points despite the fact that the diesters of this invention have higher molecular weights. It is surprising that the diesters of this invention have so many of the properties required for base fluids to be used to prepare lubricant compositions suitable for use in the most advanced jet engines.

It will be noted that the pour points for diesters of tripropylene glycol are lower than the corresponding diesters of dipropylene glycol, tetrapropylene glycol and polyethylene glycols. Accordingly, lubricant compositions of the present invention are characterized by improved low-temperature characteristics.

EXAMPLE II.

The following are excellent lubricant compositions. The antioxidant in each composition is the antioxidant mixture of Example I.

Composition	Base Fluid	% Antioxidant
(1)	Tripropylene glycol diesters containing fatty acyl groups having the following approximate random distribution: C_6-4%; C_8-55%; C_{10}-40%; and C_{12}-1% (TPGDE)	2.0
(2)	Tripropylene gylcol dipelargonate (TPGDP)	2.5
(3)	Tripropylene glycol dicaprylate (TPGDC)	1.5
(4)	Tripropylene glycol diheptanoate (TPGDH)	3.0
(5)	Tripropylene glycol dicaprate (TPGD Caprate)	1.8
(6)	1:1 mixture of TPGDP and TPGDC	2.6
(7)	30% TPGDE and 70% trimethylol propane tripelargonate (TPT)	2.0

Composition	Base Fluid	% Antioxidant
(8)	40% TPGDE and 60% pentaerythritol tetraester containing 20% C_5, 45% C_7, 15% C_9 and 20% C_{10} acyl groups (PTE)	1.5
(9)	20% TPGDE: 30% TPT and 50% PTE.	3.2
(10)	70% TPGDE and 30% dioctyl adipate	2.9
(11)	80% TPGDE and 20% di(2-ethylhexyl) sebacate	4.1
(12)	35% TPGDE and 65% of the condensation product of polyethylene glycol (n=4) and adipic acid terminated with 2-ethylhexanol (ATCE)	3.0
(13)	25% TPGDE and 75% of the condensation product of sebacic acid and polyethyleneglycol (n=5) terminated with pelargonic acid (PTCE)	2.6
(14)	20%TPGDE; 50% PTE; and 30% PTCE	2.4
(15)	20% TPGDE; 50% PTE; and 30% ATCE	1.8
(16)	30% TPGDE and 70% of the condensation product of sebacic acid and polypropylene glycol (n=3) terminated with caprylic acid (CTCE)	1.6
(17)	TPGDE	2.4
(18)	80% TPGDE and 20% dinonyladipate	2.2

EXAMPLE III.

The following are ecellent lubricant compositions. The named additives are added to the composition comprising TPG and antioxidant described in Example I, replacing an equivalent amount of base fluid.

Composition	Additive	% Additive
1.	disalicylidene-1,2-diaminepropane	.01
2.	benzoguanamine	.009
3.	thiourea	.312
4.	N-butylbenzoguanamine	.214
5.	octadecyl amine	.12
6.	quinazarin	.025
7.	quinoline	.4
8.	phenylacridine	.3
9.	hexamethylenetetramine	.24
10.	thiobenzamide	.16
11.	benzothiazole	.28
12.	imidazoline	0.111
13.	1:10 mixture of benzoguanamine and tetraoctadecyl methylenedisphosphonate	2.2
14.	1:10 mixture of quinazarin and tricresylphosphate	4.4
15.	1:1 mixture of quinoline and naphthalene	0.8
16.	Polymer of methacrylic acid esters (Acryloid 704)	0.5
17.	Polymer of methacrylic acid esters (Acryloid 714)	0.6

EXAMPLE IV.

The following are excellent lubricant compositions. The named base fluids are substituted in the indicated amounts for the base fluid of the composition comprising TPG and antioxidant described in Example I.

Composition	Base Fluid	%
1.	Allyl laurate	10
2.	Propyl propionate	15
3.	Trioctyl phosphate	20
4.	Dioctyl carbonate	10

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Composition	Base Fluid	%
5.	Isopropyl myristate	20
6.	Stearyl acetate	25
7.	Dibutyl ether of ethylene glycol	5
8.	Glycerol	5
9.	Naphthalene	6
10.	Petrolatum	10
11.	Paraffin wax	10
12.	1:1 mixture of naphthalene and xylene	7
13.	Dioctylphthalate	8.5
14.	Propylene glycol	7.2
15.	Methyl ethyl ketone	4.6
16.	Carnauba wax	9.2
17.	Tallow	4.1
18.	Stearyl alcohol	12.5
19.	20% Emulsion of tallow in water	90
20.	Octyl tripropylene glycol ether	24
21.	Mineral oil S.A.E. 10	13.1
22.	Rosin	2.6
23.	1:1 Phenol-formaldehyde resin (M.W. 1200)	4.7
24.	Grease (lubricating oil thickened with soap)	8.6
25.	Isopropyl laurate	22
26.	1:1 mixture of isopropyl and alcohol	3
27.	Kerosene	14
28.	Turbine oil	12.9
29.	40% soybean oil in water emulsion	80
30.	Di(2-ethylhexyl)sebacate	21
31.	10% suspension of graphite in mineral oil S.A.E. 10	70
32.	Polyethyleneglycol (M.W. 1800)	40
33.	Polypropyleneglycol (M.W. 2200)	30
34.	Octyl ether of polyethyleneglycol (M.W. 4000)	28
35.	Di-2-ethylhexanoate of 1:1 ethylene glycol propylene glycol (M.W. 6000)	8.9
36.	Stearyl stearate	11
37.	20% cottonseed oil in water emulsion with 5% alkyl (C_{11-15}) poly ethoxylate (9 moles) emulsifier	70
38.	Winterized and hardened (I.V. 8) soybean oil	8
39.	Naphthenic hydrocarbon oil	14
40.	Fluorinated polypropylene (M.W. 1000)	10
41.	Di-n-butylphthalate	4
42.	1:1 mixture of Di(2-butoxyethyl)azelate and di(methylcyclohexyl)adipate	20
43.	The condensation product of propylene glycol, ethylene glycol, phthalic acid and sebacic acid in a 3:2:1 ratio (M.W. 2000)	25
44.	The C_8—C_{10} Oxo alcohol esters of phthalic acid	26
45.	Butyl ether of polyethylene glycol (M.W. 1000)	9
46.	A 3:1 mixture of butyl ether of polypropylene glycol (M.W. 1600) and di-isooctyl adipate	13
47.	Dioctylpentadecandicarboxylate	19
48.	Dimethylsilicone polymer (M.W. 3000)	3
49.	Mineral Oil S.A.E. 30	22
50.	Petroleum wax	4
51.	Kendall base oil (S.A.E. 10)	17
52.	Kendall base oil (S.A.E. 10)	9
53.	Cottonseed oil	2
54.	Bis(2-ethylhexyl)sebacate	4
55.	Kendall base oil (S.A.E. 10)	23
56.	Bis(2-ethylhexyl)adipate	26
57.	Decyl decanoate	17.5
58.	Naphthalene	11.5
59.	Soybean oil	12.7
60.	Paraffin	2.3

The preparation of the diesters of the present invention may be carried out by methods analogous to the well-known, laboratory and industrial methods used for the preparation of the diesters of ethylene glycol and polyethylene glycols. These methods are described in "Fatty Acids, Their Chemistry, Properties, Production and Uses", K. S. Markley, Interscience Publishers, New York 1961—Part 2, pages 787—797.

The following Example describes a specific preparation of the diester of tripropylene glycol and C_7—C_9 fatty acid.

EXAMPLE V.

230.5 gms. (1.2 moles) tripropylene glycol and 399.6 gms. (2.7 moles) C_7—C_9 fatty acid, 300 ml. toluene and 0.1 gm. para-toluene sulphonic acid were placed in a three neck, 2 litre round bottomed flask fitted with a stirrer, thermometer and Dean-Stark water separator, topped with a reflux condenser. The mixture was heated to reflux. When 45 ml. of water had collected in the Dean-Stark separator the reaction was terminated. The toluene was distilled off at reduced pressure with a water aspirator and excess fatty acid was removed by vacuum distillation. The residue was dissolved in hexane and filtered through activated charcoal. The hexane was removed by distillation, the final traces being stripped at reduced pressure.

WHAT WE CLAIM IS:—

1. A lubricant composition comprising at least one fatty acid diester of tripropylene glycol, wherein each fatty acid moiety contains from 6 to 10 carbon atoms, and from 0.001 to 5% by weight of an antioxidant that is a mixture of p,p¹-dioctyldiphenylamine and N-phenyl-1,2,3,4-tetrahydro-2-naphthylamine.

2. A composition according to claim 1 wherein the antioxidant mixture contains from 30% to 80% by weight of the antioxidant mixture of N-phenyl-1,2,3,4-tetrahydro-2-naphthylamine.

3. A composition according to claim 1 wherein the antioxidant mixture contains from 50% to 70% by weight of the antioxidant mixture of N-phenyl-1,2,3,4-tetrahydro-2-naphthylamine.

4. A composition according to claim 1 wherein the p,p¹-dioctyldiphenylamine and N - phenyl - 1,2,3,4 - tetrahydro - 2 - naphthylamine are present in the weight ratio 2:3.

5. A composition according to any of claims 1 to 4 wherein the antioxidant constitutes 0.1% to 2% by weight of the lubricant composition.

6. A composition according to claim 5 wherein the antioxidant constitutes 1.5% by weight of the lubricant composition.

7. A composition according to any of claims 1 to 6 wherein each fatty acid group contains 7, 8 or 9 carbon atoms.

8. A composition according to any of claims 1 to 6 comprising a mixture of fatty acid diesters of tripropylene glycol in which 4% of the fatty acid groups contain 6 carbon atoms, substantially 55% of the fatty acid groups contain 8 carbon atoms, substantially 40% of the fatty acid groups contain 10 carbon atoms and substantially 1% of the fatty acid groups contain 12 carbon atoms.

9. A composition according to any of claims 1 to 6 wherein the diester is tripropylene glycol dipelargonate.

10. A composition according to any of claims 1 to 6 wherein the diester is tripropylene glycol dicaprylate.

11. A composition according to claim 1 substantially as hereinbefore described and/or exemplified.

12. A process of lubricating two frictionally engaged metal surfaces which comprises disposing between the said metal surfaces a lubricant composition, according to any of claims 1 to 11.

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